การดูดซับตะกั่วและแคดเมียมไอออนจากสารละลายโดยใช้ขุยมะพร้าว

Adsorption of Lead and Cadmium Ions from Aqueous Solution Using Coconut Coir Pith

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บทคัดย่อ

งานวิจัยนี้เป็นการศึกษาการดูดซับไอออนของตะกั่วและแคดเมียมจากสารละลายโดยใช้ขุยมะพร้าว ผลการศึกษาพบว่า สภาวะที่เหมาะสมในการดูดซับ คือ ที่ค่า pH เท่ากับ 5 ระยะเวลาสัมผัส 30 นาที ความเข้มข้นของสารละลายโลหะหนักเริ่มต้น 50 มิลลิกรัมต่อลิตร และอุณหภูมิ 30 องศาเซลเซียส ผลการทดลองสอดคล้องกับแลงเมียร์ไอโซเทอร์มแสดงให้เห็นว่าการดูดซับตะกั่วและแคดเมียมอยู่ในรูปแบบการดูดซับแบบชั้นเดียว ที่มีความสามารถในการดูดซับสูงสุดที่ 10.5 และ 5.1 มิลลิกรัมต่อลิตร ตามลำดับ และผลการศึกษาจลนศาสตร์พบว่า สอดคล้องกับสมการ pseudo-second-order แสดงว่า ขั้นตอนการดูดซับทางเคมีเป็นขั้นตอนที่ควบคุมอัตราการเกิดปฏิกิริยาที่มีผลต่อกลไกการดูดซับตะกั่วและแคดเมียมที่เกิดขึ้น นอกจากนี้ ประสิทธิภาพการคายซับตะกั่วและแคดเมียของขุยมะพร้าวมีค่าเท่ากับร้อยละ 4.56 และ 5.22 เมื่อใช้สารละลายกรดไฮโดรคลอริกเข้มข้น 1 โมลาร์ ซึ่งแสดงว่าขุยมะพร้าวที่ผ่านการ ดูดซับเหมาะสมที่จะถูกนำไปฝังกลบอย่างปลอดภัย เนื่องจากโอกาสจะปลดปล่อยลงสู่สิ่งแวดล้อมต่ำ จากผลการทดลองทั้งหมด สามารถสรุปได้ว่า การใช้ขุยมะพร้าวเป็นตัวดูดซับจัดเป็นการใช้วัสดุเหลือทิ้งที่มีประโยชน์ เป็นการจัดการวัสดุเหลือทิ้ง และเป็นแนวทางที่เป็นมิตรกับสิ่งแวดล้อม

คำสำคัญ : การดูดซับ ตะกั่ว แคดเมียม ขุยมะพร้าว

Abstract

This research investigated the adsorption of lead and cadmium ions from aqueous solution using coconut coir pith (CCP). The results indicated that the optimal condition consisted of pH 5, 30 minutes of contacting time, 50 mg/l of initial concentration, and 30°C of temperature. The experimental data were well fitted with Langmuir isotherm. It explained that Pb^{2+} and Cd^{2+} adsorbed in form of monolayer. The adsorption maximum capacities of CCP were 10.5 mg/g and 5.1 mg/g of Pb^{2+} and Cd^{2+}, respectively. Then, adsorption kinetics was suitable to explain using pseudo-second-order model. The results intended that the mechanism of Pb^{2+} and Cd^{2+} adsorption by CCP depend on the rate controlling step due to chemical sorption. In addition,

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desorption efficiencies were 4.56% at 5.22% at 1 M HCl. The results elucidated that spent CCP was suitable to deposit in secure landfill because Pb^{2+} and Cd^{2+}adsorbed could be released very low. Finally, using of CCP are adsorbents as waste utilization, waste management, and eco-friendly approach.

Keywords: adsorption, Pb^{2+}, Cd^{2+}, coconut coir pith

Introduction

As a result of rapid industrialization, toxic metals and metalloid such as cadmium, lead, chromium, mercury, arsenic and copper are released into the environment resulting in damage in ecosystems and human health[1]. Lead uses many industries such as acid battery manufacturing, metal plating and finishing, printing, photographic materials, explosive manufacturing, and tetraethyl lead manufacturing, and ceramic and glass industries. The main sources of lead in water are the effluents of processing industries. Lead poisoning in humans causes severe damage to the kidney, nervous system, reproductive system, liver, and brain and causes sickness or death. Severe exposure to lead has been connected with sterility, abortion, stillbirths, and neonatal death[2-5]. In the other hand, cadmium ion (Cd^{2+}) may be found in wastewater discharges from the electroplating industry, the manufacture of nickel–cadmium batteries, fertilizers, pesticides, pigments and dyes and textile operations[6-7]. The serious incident of itai-itai disease in Japan was due to cadmium ions. The harmful effects of Cd^{2+} ions are renal damage, hypertension, proteinuria, kidney stone formation and testicular atrophy. Cd^{2+} ions may replace Zn^{2+} ions in some enzymes, thereby affecting the enzyme activity[8-9]. Because of its effects, many scientists and researchers have used various techniques for reducing lead from wastewater including chemical precipitation[10,11], coagulation[12], membrane[13,14], electrodialysis[15,16] or adsorption[10]. Among these techniques, adsorption has been proposed as a cost-effective method. However, activated carbon which is widely used as an effective adsorbent in many applications is relatively expensive and use high energy in the preparation process because it is usually prepared at more than 600^0C[17,18]. Thus, agricultural wastes such as leaves of date trees[19], *Euphorbia rigida*[20], coffee grounds and wheat straw[21], saw dust[22], coir pith[23], and rice husk[24] have been interested to use for Pb^{2+} or Cd^{2+} adsorption. In this research, researchers use CCP to be adsorbent. CCP is a lignocelluloses materials which normally contains a variety of organic compounds (lignin, cellulose and hemicelluloses) and functional groups (hydroxyl and carboxylic). Thus, this research investigated adsorption of Pb^{2+} and Cd^{2+} using coconut. In the research, adsorption factors as pH, contact time, initial Pb^{2+} and Cd^{2+} concentration, and temperature were studied and theirs results were analyzed to study adsorption isotherms and kinetics. Finally, desorption was investigated to determine the appropriate method for spent adsorbent management.

Material and Methodology

Preparation of Pb^{2+} and Cd^{2+} solution

Lead nitrate ($Pb(NO_3)_2$) 1.6 g was dissolved in distilled water and adjusted to be 1,000 mL. In the other hand, Cadmium nitrate ($Cd(NO_3)_2.4H_2O$) 2.74 g was dissolved in distilled water and adjusted to be 1,000 mL. For this purpose, the concentration of Pb^{2+} and Cd^{2+} solution was 1,000 mg/L as the main or stock solution which was contained to container for using in all experiments. Then, the other Pb^{2+} and Cd^{2+} concentrations were prepared by diluting the main solution. Furthermore, 0.1 M HNO_3 and 0.1 M NaOH were used to adjust pH of solution. All used chemicals were in AR grade. It is important to note that all the experiments were triplicate.

Preparation of coconut coir pith

Coconut coir pith was a by-product from coconut milk community industries in Maha Sarakham, Thailand. It was washed by distilled water until pH of effluent water equal to influent water for removing contaminated substances. Then, washed coconut coir pith was dried in oven at 105 ^{0}C for 24 hours. Finally, dried coconut coir pith is contained in a container for using in all experiments.

Adsorption experiments

All batch adsorption experiments were carried out in a 250 mL flask containing 100 mL the solution in an incubator shaker with a shaking speed of 150 rpm. For each treatment, 0.5 g (5 g/L) of adsorbents was added and shaken for specified period. The concentrations of metal ion were determined by Atomic Absorption Flame Emission Spectrophotometer (AAS) (model AA-6200, Shimadzu) at 283.3 nm for Pb^{2+} and 228.8 nm for Cd^{2+}. The adsorption efficiency and capacity was calculated according to the equation (1) – (2)[25]. Furthermore, desorption efficiency was determined according to the equation (3)

Adsorption efficiency (%)

$$= ((C_I – C_f)/m) \times 100\% \quad (1)$$

Adsorption capacity (mg/g)

$$= (C_i – C_f)/m) \times V \quad (2)$$

Desorption efficiency (%)

$$= \{[C_e - (C_i – C_f)]/(C_i – C_f)\} \times 100\% \quad (3)$$

Where C_i = the initial concentration of metal ion in the solution (mg/L), C_f = the residual metal ion concentration, C_e = the equilibrium metal ion concentration, and V = the volume of metal ion (L), and m was the amount of adsorbent used (CCP) (g)

The adsorbent (CCP) were used to study the effects of pH (2.0 – 7.0), contact time (0, 5, 10, 15, 30, 60, 120, 240 and 360 min), initial metal ion concentration (5, 10, 25, 50 and 100 mg/L) and temperature (30^{0}C, 45^{0}C, and 60^{0}C). The pH was adjusted using 0.1 M HNO_3 and 0.1 M NaOH

Isotherm experiments were conducted with different initial metal ion concentrations (5 – 100 mg/L) for equilibrium time. The experiments were carried out at different temperatures of 30^{0}C, 45^{0}C, and 60^{0}C, respectively. The experimental data was fitted into the following isotherms: Langmuir and Freundlich[20].

The Langmuir isotherm is valid for monolayer adsorption onto a surface containing a finite number of identical sites. The model assumes uniform energies of adsorption onto the surface and no transmigration of adsorbate in the plane of the surface. Based upon these assumptions, Langmuir represented the following equation:

$$C_e/q_e = (1/q_m)\, C_e + (1/q_m b) \quad (4)$$

$$1/q_e = (1/q_m b)\, C_e + (1/q_m) \quad (5)$$

Where: q_e = the amount of metal adsorbed per gram of the adsorbent at equilibrium (mg/g), q_m = maximum monolayer coverage capacity (mg/g), and b = Langmuir isotherm constant (L/mg). The essential features of the Langmuir isotherm may be expressed in terms of equilibrium parameter R_L, which is a dimensionless constant referred to as separation factor or equilibrium parameter.

$$R_L = 1/(1+(1+bC_i)) \quad (6)$$

Where: b = the constant related to the energy of adsorption (L/mg), and R_L value indicates the adsorption nature to be either unfavourable if $R_L>1$, linear if $R_L=1$, favourable if $0< R_L<1$ and irreversible if $R_L=0$.

Freundlich Adsorption Isotherm is commonly used to describe the adsorption characteristics or the heterogeneous surface. These data often fit the empirical equation proposed by Freundlich:

$$q_e = K_f C_e^{1/n} \quad (7)$$

$$\log q_e = \log K_f + 1/n \log C_e \quad (8)$$

Where K_f = Freundlich isotherm constant (mg/g) and n = adsorption intensity. The constant K_f is an approximate indicator of adsorption capacity, while 1/n was a function of the strength of adsorption in the adsorption process. If n = 1 then the partition between the two phases are independent of the concentration. If value of 1/n is below one it indicates a normal adsorption. On the hand, 1/n being above one indicates cooperative adsorption.

Adsorption Kinetics[26]

Adsorption kinetics of Pb^{2+} and Cd^{2+} onto CCP was studied using pseudo-first-order and pseudo-second-order kinetic equations according to equation (9) and (10), respectively.

$$\log (q_e - q_t) = \log q_e - (k_1/2.303)\, t \quad (9)$$

Where q_t (mg/g) are the amount of metal ion adsorbed on CCP at time t (min). k_1 (1/min) is the pseudo-first-order rate constant

$$1/q_t = (1/k_2 q_e^2) - (1/q_e)\, t \quad (10)$$

Where k_2 (g/mg.min) is the rate constant.

Results and Discussion

Effects of pH on Pb^{2+} and Cd^{2+} adsorption

The acidity of solution pH is one of the most important parameters controlling the uptake of heavy metals from wastewater and aqueous solutions[2]. The uptake and percentage removal of Pb^{2+} and Cd^{2+} from the aqueous solution are strongly affected by the pH of the solution as illustrated in Figure 2.

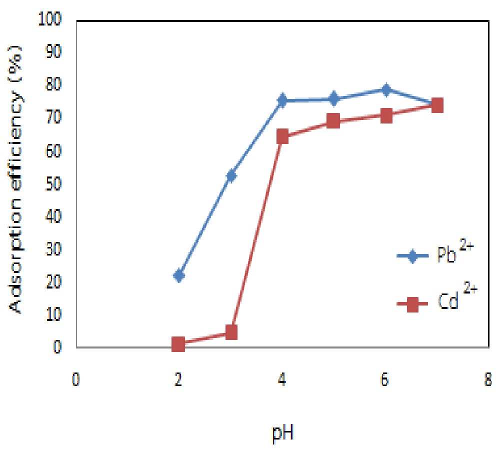
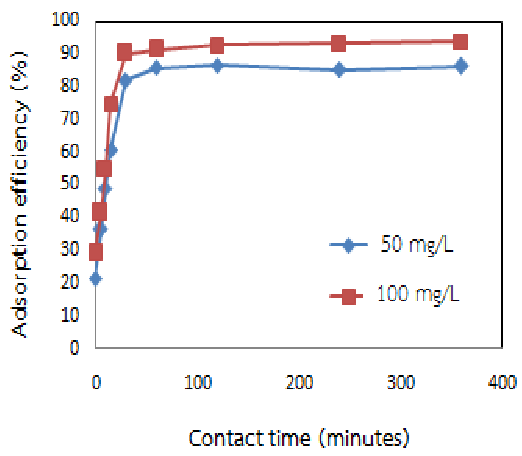


Figure 2 Effects of pH on adsorption efficiency

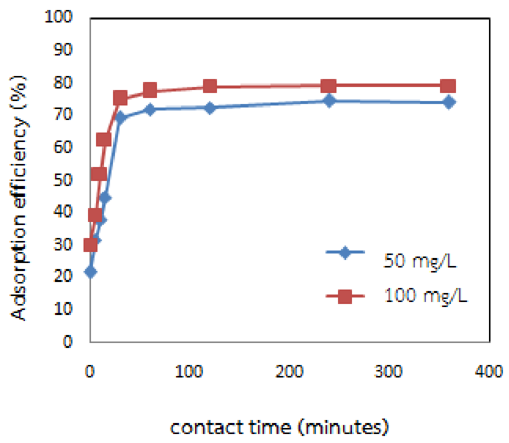
From this graph, the lower percentage removal of Pb^{2+} and Cd^{2+} at a low pH is due to the low number of deprotonated sites, providing a smaller number of sites for the adsorption of Pb^{2+} and Cd^{2+}[27]. Moreover, at lower pH, the presence of excess H^+ ions in the solution competes with Pb^{2+} and Cd^{2+} ions for the adsorption sites. The former are adsorbed more than the latter owing to the high concentration and high mobility of H^+ ions, whereas in the higher pH range there are fewer competing H^+ ions and the surface of the adsorbent may become negatively charged owing to higher deprotonation, which enhances the adsorption of positively charged Pb^{2+} and Cd^{2+} ions through electrostatic forces of attraction[28]. In both cases, the optimal pH was found to be 5, which was used for further adsorption experiments in the present study. At higher pH 5, Pb^{2+} and Cd^{2+} were transformed and precipitated in form of $Pb(OH)_2$ and $Cd(OH)_2$. Therefore, the results can't discuss that they occurred from the effects of adsorption process only.

Effects of contact time and concentration

This experiments were conducted with two initial metal ion concentration (50 and 100 mg/L) with a dose of 5 g/L CCP at 150rpm and 30^{0}C for 0, 5, 10 ,15, 30, 60, 120, 240, and 360 minutes. Figure 5 elucidated the effects of contact time on adsorption of Pb^{2+} and Cd^{2+} using CCP



(a)



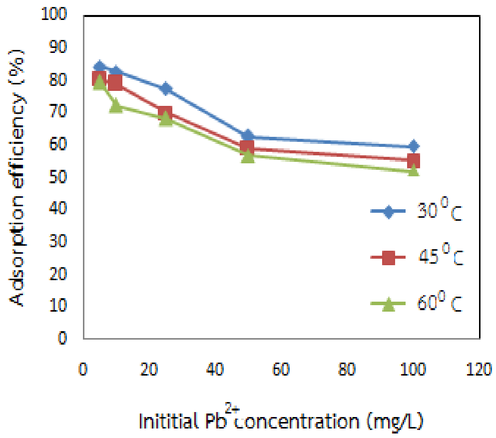
(b)

Figure 3 Effects of contact time on adsorption efficiency (a) Pb^{2+} (b) Cd^{2+}

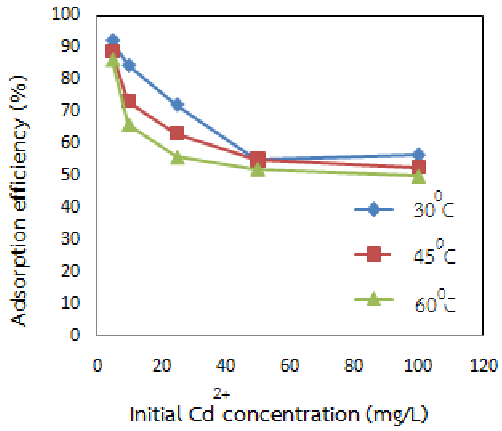
Adsorption rate of $Pb^{2+}$and Cd^{2+} on CCP was found to be relatively much faster than those reported for some other bio-adsorbents. The rate of Pb^{2+} removal was very rapid during the first 30 min, and thereafter, the rate of removal remained constant. There was no significant increase in adsorption after about 30 min. Initially, there were large number of vacant active binding sites in CCP and consequently large amount of Pb^{2+} and Cd^{2+} ions were bound rapidly onto CCP. The binding site was shortly become limited and the remaining vacant surface sites are difficult to be occupied by ions due to the formation of repulsive forces between the copper on the solid surface and the liquid phase[29]. At 30 minutes of contact time, adsorption rate is equal to desorption rate which this condition is "equilibrium condition". Therefore, the equilibrium time is 30 minutes. In the addition, adsorption efficiency of each concentration was different. It can be conclude that the concentrations have effects to the adsorption.

Effects of Initial Pb^{2+} and Cd^{2+} concentration and temperature

This experiments were conducted with initial $Pb^{2+}$and Cd^{2+}concentration (5, 10, 25, 50 and 100 mg/L) with a dose of 5 g/L CCP at 150 rpm and 30^{0}C, 45 ^{0}C, and 60 ^{0}C Figure 6 showed the effects of contact time on adsorption of $Pb^{2+}$and Cd^{2+} using CCP.



(a)



(b)

Figure 4 (a) and (b) Effects of initial Pb^{2+} and Cd^{2+} concentrations on CCP

The figure elucidated that the adsorption capacity or the amount of Pb^{2+} and Cd^{2+} adsorbed per gram increased with the increase of initial Pb^{2+} and Cd^{2+} concentration. This increase could be due to an increase in electrostatic interactions (relative to covalent interaction), because the electrostatic field exits in around CCP particles[30]. Moreover, it decreased with the increase of temperature so the adsorption of Pb^{2+} and Cd^{2+} were the exothermic reaction[31-33].

Adsorption Isotherms

Adsorption isotherm experiments were conducted with different initial metal ion concentration (5 – 100 mg/L) for equilibrium time. The experiments were carried out at different temperatures of 30^{0}C, 45^{0}C, and 60^{0}C, respectively. The experimental data was fitted into the following isotherms: Langmuir and Freundlich. The adsorption equilibrium constants were determined and

Table 1 Adsorption equilibrium constants obtained from Langmuir and Freundlich isotherms (Pb^{2+})

Temperature (^0C)	**Langmuir Constants**			**Freundlich Constants**		
	q_m (mg/L)	**b (L/mg)**	**R^2**	**n**	**K_f (mg/L)**	**R^2**
30	10.504	0.110	0.998	0.64	1.091	0.987
45	9.541	0.094	0.997	0.65	1.133	0.994
60	7.304	0.094	0.976	0.67	1.298	0.996

Table 2 Adsorption equilibrium constants obtained from Langmuir and Freundlich isotherms (Cd^{2+})

Temperature (^0C)	**Langmuir Constants**			**Freundlich Constants**		
	q_m (mg/L)	**b (L/mg)**	**R^2**	**n**	**K_f (mg/L)**	**R^2**
30	5.099	13.782	0.935	0.50	1.385	0.979
45	4.306	0.426	0.873	0.55	1.016	0.971
60	3.780	0.409	0.823	0.57	1.116	0.948

The conditions might coexist under the experimental conditions, but monolayer adsorption was more dominant. Moreover, q_m decreased of the increasing of the temperature. Therefore, the adsorption process of Pb^{2+} and Cd^{2+} using CCP is exothermic reaction. In Comparing the maximum capacity of Pb^{2+} and Cd^{2+} removal with the previous study (shown in Table 4), CCP was one of adsorbents which is interesting.

Table 3 Comparison of the maximum Pb^{2+} and Cd^{2+} adsorption capacity (q_m) of various adsorbents

Absorbent	**Adsorbate**		**q_m (mg/g)**	**Reference**
	Pb^{2+}	**Cd^{2+}**		
Okra wastes	/		5.74	[34]
Almond shells	/		2	[35]
Luffa cylindica Fiber	/		4.63	[36]
Coconut coir pith	/		10.5	This research
Sawdust		/	5.76	[37]
Baggasse fly ash		/	6.19	[38]
Olive cores		/	7.73	[39]
Coconut coir pith		/	5.1	This research

Adsorption kinetics

Adsorption kinetics of Pb^{2+} and Cd^{2+} onto CCP was studied using pseudo-first-order and pseudo-second-order equations according to equation (16) - (18), respectively. Theirs results were showed in Table 4

Table 4 Pseudo-first-order model and Pseudo-second-order model

Adsorbent	Pseudo-first-order model			Pseudo-second-order model		
	k_1 (1/min)	q_e (mg/g)	R^2	k_2 (g.mg^1.min)	q_e (mg/g)	R^2
Pb^{2+} – 50 mg/L	0.069	6.27	0.989	0.029	8.77	0.999
Pb^{2+} – 100 mg/L	0.088	13.92	0.912	0.033	15.15	0.993
Cd^{2+} – 50 mg/L	0.072	1.35	0.665	0.04	4.15	0.998
Cd^{2+} – 100 mg/L	0.035	7.21	0.247	1.10	3.22	0.944

In Table 5, the results displayed that the experimental data fitted well with Pseudo-second-order model. Therefore, it indicated that the mechanism of Pb^{2+} and Cd^{2+} sorption by CCP depend on the rate controlling step due to chemical sorption[37].

Desorption Study

In this experiment, spent adsorbents from the optimal condition were leached by 0.1, 0.5, and 1.0 M HCl. The mixture between spent adsorbent and leaching solution was mixed at 150 rpm and 30^{0}C for 30 minutes. Desorption efficiency was calculated using equation (3) and the results was showed in Figure 5. This line graph elucidated that Pb^{2+} and Cd^{2+} on CCP could be released very low. Therefore, spent CCP was suitable to deposit in the secure landfill.

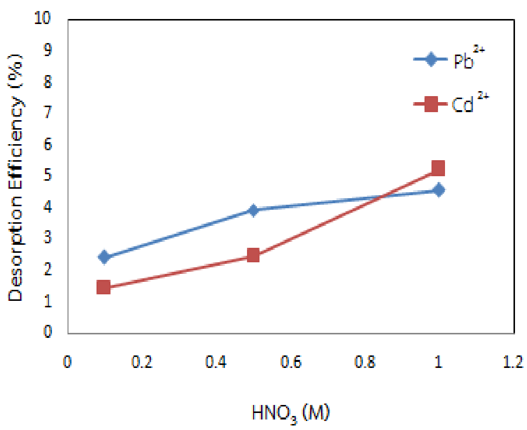


Figure 5 Desorption efficiency of Pb^{2+} and Cd^{2+} on CCP

Conclusion

The results indicated that the optimal condition consisted of pH 5, 30 minutes of contacting time, 50 mg/l of initial concentration, and 30°C of temperature. The experimental data were well fitted with Langmuir isotherm. It explained that Pb^{2+} and Cd^{2+} adsorbed in form of monolayer. The adsorption maximum capacities of CCP were 10.5 mg/g and 5.1 mg/g of Pb^{2+} and Cd^{2+}, respectively. Then, adsorption kinetics was suitable to explain using pseudo-second-order model. The results intended that the mechanism of Pb^{2+} and Cd^{2+} adsorption by CCP depend on the rate controlling step due to chemical sorption. In addition, desorption efficiencies were 4.56% at 5.22% at 1 M HCl. The results elucidated that spent CCP was suitable to deposit in secure landfill because Pb^{2+} and Cd^{2+}adsorbed could be released very low.

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